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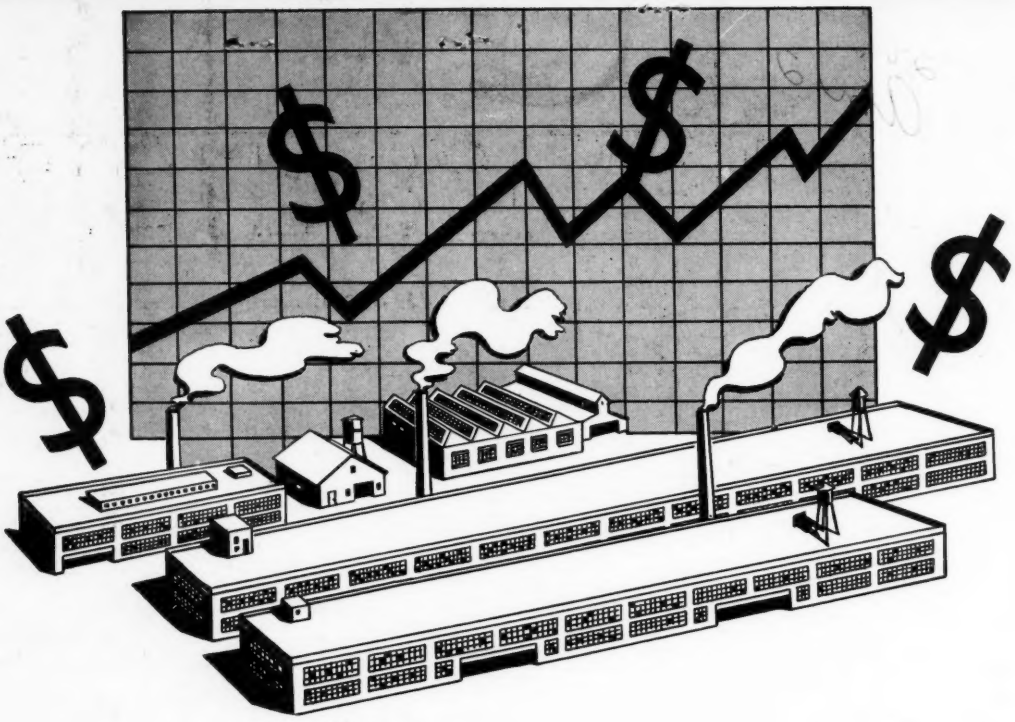

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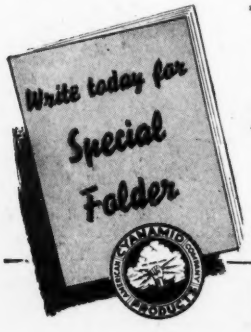

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American Dyestuff Reporter, Vol. 30, No. 18, September 1, 1941. Published every other Monday. Copyright, 1941, by Howes Publishing Co. 440 4th Ave.,

AMERICAN DYESTUFF REPORTER

A. P. HOWES
Publisher

LOUIS A. OLNEY
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Official Publication of the Proceedings of the American Association of Textile Chemists and Colorists

SEPTEMBER, 1, 1941

VOLUME 30 NUMBER 18

American Dyestuff Reporter, Vol 30, No. 18, Sept. 1 1941. Published every other Monday. Copyright, 1941, by Howes Publishing Co., 440 4th Ave., New York, N. Y. Domestic subscription, $5.00, Canadian, $6.00, Foreign, $6.00. Entered as second-class matter, Nov. 6, 1919, at the New York, N. Y. Post Office, under the act of March 3, 1879.

Contents

Contents of previous issues can be found by consulting the Industrial Arts Index at your library

• Special Articles

Microscopic Structure of the Wool Fiber..... 449
Charles W. Hock, Robert C. Ramsay and Milton Harris

Theoretical and Practical Aspects of Cationic Finishing Agents 461
Robert R. Ackley

Division of Cellulose Chemistry of the American Chemical Society—Abstracts of Papers..... 465

• Proceedings of the American Association of Textile Chemists and Colorists

Report of the Nominating Committee..... P457

Outing, Philadelphia Section..... P460

Calendar of Coming Events..... P460

• Departments

Trade Notes—New Products..... 463

Technical Notes from Foreign Sources..... 467

Open Forum 470

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CONTENTS

	Page
Foreword	3
How to Use the Dye Cost Book	5
Dye Costs by Ounces from $ .50 to $5.00 per Pound	9 to 33
Dye Costs by Pounds from $ .11 to $3.00 per Pound	34 to 43
Comparison of the Baumé Hydrometer Scale	44
Conversion Tables	44 to 47
Degrees Baumé into Degrees Twaddle (Conversion Table)	44
Degrees Twaddle into Degrees Baumé (Conversion Table)	45
Decimal Percentages into Avoirdupois Weight (Conversion Table)	46
Degrees Fahrenheit to Degrees Centigrade (Conversion Table)	46
Dye Cost Per Hundred Pounds to Cost Per Yard (Conversion Table)	46
Ounces, Grams, Grains (Conversion Table)	46
Textile of 1% to Ounces Per 100 Pounds (Conversion Table)	47
Dye Required Per Weight of Material (Conversion Table)	47
pH Range of Indicators	48
Fastness Scales	48
Hardness of Water and Its Effects	49 and 50
Chemicals Used in Textile Processing	51 to 59
Dyes and Current Prices	60 to 63
Chemicals and Current Prices	64 to 68
Notes	

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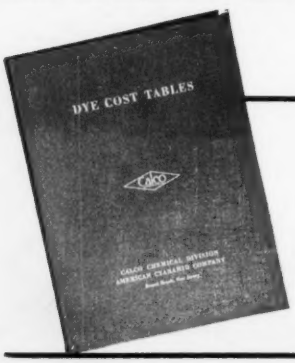

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Microscopic Structure of the WOOL FIBER

CHARLES W. HOCK, ROBERT C. RAMSAY, and MILTON HARRIS*

Abstract

An investigation was undertaken to obtain information concerning the fine details of structure of wool fibers and especially of their constituent scale and cortical cells. Treatment of chemically modified wool with the enzyme, pepsin, was found to be an excellent method for releasing individual cells for such studies.

It is shown by microdissection that the striated appearance of the cortical cells is due to the presence of many fibrils which can be separated with microneedles. Near the center of each cell is a nucleus which has a granular structure. Between crossed nicols, the fibrillar part of the cortical cells appears birefringent, whereas the nucleus does not.

The scales show little internal organization such as exhibited by the cortical cells. When examined with crossed nicols they appear nonbirefringent. Unlike the cells of the cortex, the scales are not easily separated by treatment with enzymes, but remains attached to each other in a manner comparable to the arrangement of shingles on a roof.

A comparison of root and shaft of the fiber reveals numerous differences in reaction to microchemical color tests, as well as differences in cellular structure. The root, for example, gives a positive test for sulfhydryl groups whereas the shaft gives a negative test. Similarly, the shaft appears birefringent whereas the root does not. These and other observations clearly indicate that as the cells of the root emerge into the shaft a number of physical and chemical changes take place simultaneously.

When wool is placed in chlorine water bubbles arise on the surface of the fibers (Allwörden reaction). Evidence is presented in support of the viewpoint that these bubbles arise solely from the scales and that their formation is associated with the reaction of the chlorine with disulfide groups of the cystine in the scales.

I. INTRODUCTION

WOOL fibers are specialized appendages of the epidermis of the sheep, and show many similarities to other skin tissues, such as nails, horns, and feathers. A growing fiber consists of a root and shaft, the former being the living region situated beneath the surface of the skin, whereas the latter is the nonliving portion that extends above the skin surface. Increase the length of the fiber is brought about by the proliferation of new cells in the root and the subsequent emergence of these cells into the shaft. The shaft is composed of dead cellular units which usually are arranged in three layers, an outer layer of scales, a middle region called the cortex, and a central core or medulla. The relative thickness of each of these layers varies considerably in different fibers. Kemp, for example, has a large medulla, whereas in the best grades of wool the medulla is either absent or very small.

Much of this knowledge of the structure of the fiber was contributed by the early researches of Nathusius[1] and McMurtrie[2]. These investigators obtained considerable information concerning the shape, length, and fineness of wool, and in addition described the various types of cells which comprise the fiber. A number of the structural details were also noted later by Kronacher and Lodeman[3], von Bergen[4], Reumuth[5], and Müller[6] as well as others. In the present investigation these earlier observations have been extended in order to obtain additional information on the fine details of structure of the fibers and especially of their constituent cells.

II. MATERIALS

Two samples of wool were used in the investigation. One consisted of domestic wool, for the most part nonmedullated, which was purified by successive extractions

*Research Associates at the National Bureau of Standards representing the Textile Foundation.

with ethyl alcohol and with ether for 16 hours each, followed by washing with water at 40° C. A second sample was obtained from the Bureau of Animal Industry, U. S. Department of Agriculture.* It consisted of wool carefully pulled from the back of a Hampshire sheep so as to have the roots attached to the shaft, and also of small pieces of skin which were cut directly from the sheep and placed in fixing fluids.

III. EXPERIMENTAL PROCEDURE AND RESULTS

1. Separation of cortical and scale cells

When wool fibers are mounted in water and examined with a microscope, much can be learned about the size, shape, and appearance of the surface of the fibers, but very little is learned of the detailed structure of their constituent cells. In order to study the minute structure of the various types of cells, the fibers must be treated in a way that makes a more detailed microscopic examination possible. For this purpose thin cross and longitudinal sections can be employed to good advantage, but the liberation of single cells from the fibers is even more satisfactory.

The liberation of cells from fibers by various chemical reagents, enzymes, and bacteria has been frequently reported in the literature. The treatments with chemical reagents usually involve the use of strong acids or alkalies and are sufficiently drastic to produce more or less profound changes in structure. Treatment of the fibers with enzymes is in many respects more satisfactory and has been used considerably in the present investigation.

Although untreated wool is highly resistant to the action of enzymes, it has been shown in work now in progress in this laboratory[7] that fibers in which disulfide cross-linkages have been ruptured by reduction with thioglycolic acid and then methylated to prevent re-formation of the linkages are rapidly attacked by treatment with an enzyme such as pepsin. Accordingly, it was decided to follow, microscopically, the changes which reduced and methylated wool undergoes in pepsin, in an effort to obtain information concerning the structure and behavior of the cells. For comparison, untreated fibers were similarly examined.† Samples of each were placed in vials containing a solution of the enzyme. At the same time, single fibers were placed in a drop of enzyme on a microscope slide and protected with a cover glass, which was sealed to the slide with vaseline. The latter method made possible the continuous observation of a single fiber over a relatively long period. The specimens were examined and fresh enzyme was added every 2 or 3 days. The experiments were run at two temperatures, one at room temperature (22-25° C.) and another at 35° C. The material kept at the higher temperature was the first to show evidence of attack by the enzyme, but otherwise the two series ultimately presented essentially the same microscopic appearance.

In agreement with the other work[7], it was found that untreated wool was not readily attacked by pepsin. Even after long exposure to the enzyme these fibers showed little evidence of damage except for frayed ends, and sometimes the liberation of a few cortical cells. The reduced and methylated wool was attacked more rapidly. Cells obtained from this wool had the same initial appearance as cells obtained in a similar manner from untreated wool. However, as will be shown later, cells from untreated wool were resistant to further action of the enzyme whereas cells from reduced and methylated samples were eventually digested. With reduced and methylated wool, even at room temperature, changes in the fiber were detectable in less than 24 hours. The free ends of the fiber were usually frayed, and some intermediate parts appeared to be darkened and crushed. After several days pronounced changes had taken place. The fibers had lost their luster and exhibited a pronounced striated appearance due to the increased prominence of the cortical cells. After continued treatment with enzymes, large numbers of cortical cells were liberated from the fibers (Fig. 1, A, B and C). The cortical cells were removed not only from the ends of the fiber but from intermediate parts as well, leaving in extreme cases practically intact tubes of scale cells (Fig. 1, C). In regions where only part of the cortex was removed from a given area, it was found that the first cells to be liberated lay next to the scales. Additional cortical cells were released upon applying pressure to the cover glass.

The enzyme apparently had easier access to the cut ends of the fiber and thus brought about greater deterioration in those regions. This behavior has also been noted by other investigators. Photomicrographs by von Bergen[4] indicate that after certain chemical treatments the ends show the most damage. From the work of Royer and Millson[8] on dyed wool it is evident, also, that the ends of the fibers take up dye more rapidly than do intermediate parts. Similar results, indicative of the greater liability to attack at the ends, were obtained in the present investigation. Furthermore, when the ends of untreated and of reduced and methylated fibers were sealed with glue before placing the fibers in pepsin, it was found that the breakdown of the fibers was retarded. After a few weeks in the enzyme, however, this difference between fibers with sealed and with unsealed ends was lost, both samples then showing similar degrees of disintegration.

In order to study further the action of pepsin on untreated and on reduced and methylated wool, cross-sections, cut 10 to 15 microns thick with the Hardy device[9], were placed either in vials containing the enzyme or in drops of the latter on microscope slides. Even after a month there were only slight changes in the untreated sections (Fig. 2, A). With sections of reduced and methylated wool the cortex was eaten out, leaving in extreme cases only a thin ring of scales (Fig. 2, C). The degree of breakdown of the wool was related to the

*Acknowledgment is made to Dr. J. I. Hardy for supplying this material.

† A solution of pepsin was prepared by dissolving 1 mg. of the crystalline enzyme in 1 ml. of phosphate buffer at pH 1.2. A few drops of merthiolate were added to the solution as a preservative.

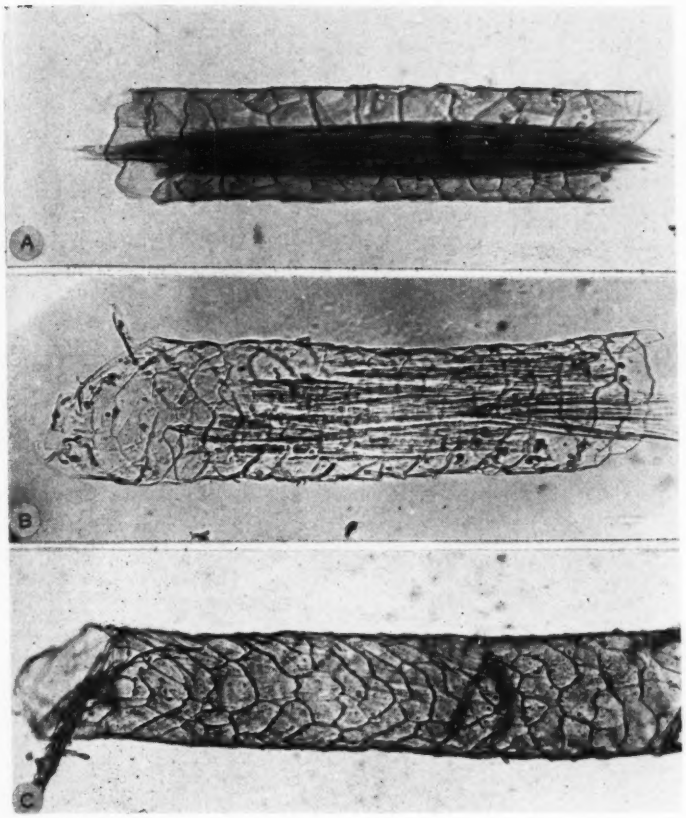

Fig. 1—Reduced and methylated wool fibers treated with solutions of pepsin. A, B, and C show three stages in the removal of cortical cells from the fibers. A and B unstained; C stained with Orange II. Magnification X 350

length of exposure to the enzyme (compare Fig. 2, B with Fig. 2, C). Furthermore, the rate of digestion appeared to be associated with the extent of reduction of the wool, as reduced and methylated fibers with 90 per cent of the disulfide cross-linkages broken were much more rapidly attacked by the enzyme than those in which only 50 per cent of the linkages had been disrupted. When free cortical cells, released from partially reduced and methylated fibers upon treatment with pepsin, were placed in fresh enzyme for a period of 1 month, some of the cells appeared to be digested whereas others from the same sample remained practically intact. These differences appear to be associated with the extent of reduction of the wool and suggest that the undigested cells may be ones in which most of the cross-links are intact.

The results of these experiments indicate that the scale cells are resistant to the action of pepsin and that the ease with which single cortical cells are liberated depends on the previous chemical treatments which the fibers received. Although cortical cells may be rapidly separated from each other by the action of pepsin, individual cells show further signs of disintegration only after continued treatment with the enzyme.

2. Structure of the cortical cells

Single cortical cells are spindle-shaped. They vary in size depending on the sample of wool. Walther[10] found that their average size varied from 80 to 110 microns in length, 2 to 5 microns in width, and 1.2 to 1.6 microns in thickness. Cortical cells liberated from fibers by the action of chemical agents frequently show evidence of fimbriated ends. In most cases, also, the cells are prominently striated.

Fig. 2—Cross sections of wool fibers treated with solutions of pepsin.
A. Sections of untreated fibers in pepsin for 1 month.
B. Sections of reduced and methylated fibers in pepsin for 10 days.
C. Section of reduced and methylated fibers in pepsin for 1 month, showing only the thin ring of scales which remains.
Magnification X 450

On careful examination of single cells liberated from the cortex by the action of pepsin, a structure located near the center of the cell and resembling a nucleus was frequently observed (Fig. 3, A). This central region did not, however stain with common nuclear dyes such as hematoxylin and methylene blue. Fig. 3, A shows also that the nucleus is granular, whereas the rest of the cell is fibrillar in appearance.

Nuclei are not easily observed in untreated cross-

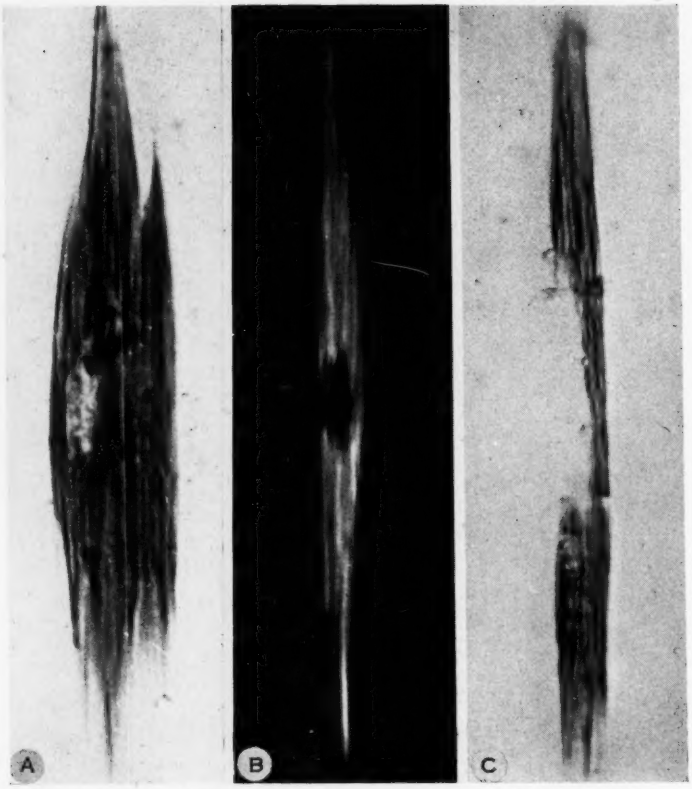

Fig. 3—Single cortical cells from reduced and methylated fibers photographed under various conditions.
A. Cell, stained with Orange II, showing the nucleus and the fibrillar appearance of the rest of the cell.
B. Cell, between crossed nicols, showing the non-birefringent nucleus in the birefringent cell.
C. Single cell nearly eaten in two by the prolonged action of pepsin. Magnification X 1400.

sections, but are clearly visible after the latter have been properly stained or swollen[5]. For example, treatment of the sections with pepsin, sodium carbonate, or with a combination of both these reagents rendered the outline of individual cortical cells and their nuclei distinct (Fig. 4). Furthermore, when the cells were treated with Orange II* (a dye which readily stains wool) the cells became deep orange, but this central region was only lightly stained. Upon examination with crossed nicols, a dark, central elongated area was nearly always detectable in the bright cell (Fig. 3, B). In other words, each birefringent cortical cell possesses a nonbirefringent nucleus. Finally after continued treatment with pepsin, many of the cortical cells were nearly eaten in two at the middle (Fig. 3, C), even though the cell is widest at this point. This suggested that the nucleus consists of a material which is more readily attacked by the enzyme than is the rest of the cell.

The structural details of the cortical cells were further investigated by dissecting them with the aid of a micromanipulator. Upon careful manipulation it was possible to insert two fine glass needles into a single cell and pull

*A 1.4 per cent solution of Orange II at pH 1.5 was used.

Fig. 4—Cross section of an untreated wool fiber after several weeks in a solution of pepsin followed by swelling with 9 per cent sodium carbonate. The photomicrograph shows the outline of the individual cortical cells and their nuclei. Magnification X 1500

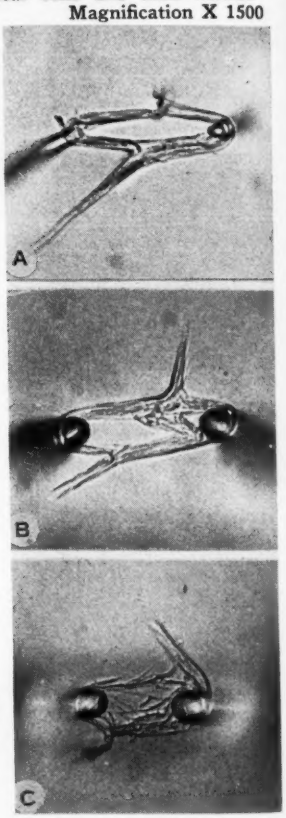

Fig. 5—Cortical cells being dissected with microneedles to show their fibrillar structure. Magnification X 500

it apart. When this was done, it was found that the cell was composed of many fibrils (Fig. 5, A, B and C). When examined between crossed nicols the latter appeared to be birefringent. Small and large groups of fibrils were dissected from the cell, and in some cases all the fibrils were spread out in the form of a fan. By this technique it was possible to prove that the striated appearance of the cortical cells is due to the presence of fibrils and not merely to surface irregularities or diffraction phenomena.

3. Structure of the Scale Cells

As already described, the scales, unlike the cells of the cortex were not appreciably affected by pepsin. They

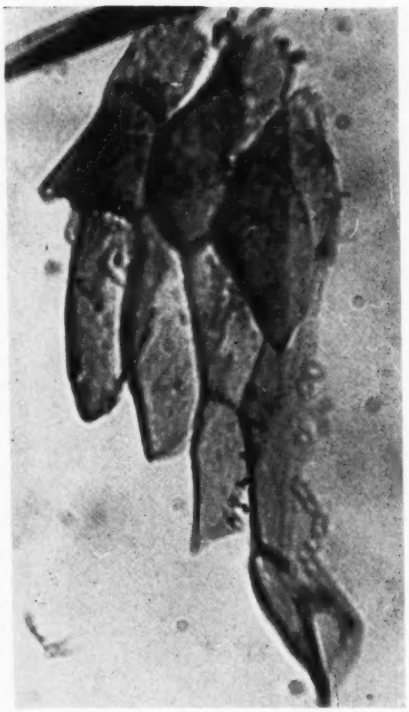

Fig. 6—Group of scales released by the action of pepsin on reduced and methylated fibers. Stained with Orange II. Magnification X 1420

Fig. 7—Single fiber (recently pulled from the back of a sheep) stained according to Feulgen's technique, showing the dark colored root indicative of a positive test for nucleic acid. Fibers mounted in water. Magnification X 120

Fig. 8—Root of a wool fiber showing individual nuclei in the cells of the root. Fiber stained according to the technique of Feulgen and mounted in tricresyl phosphate. Magnification X 500

usually remained attached to each other in the form of tubes (Fig. 1, A, B, and C) corresponding to their arrangement in intact fibers, or at least in rather large groups, which furnished excellent material for a microscopic examination. The liberation of single scale cells was relatively infrequent, nor were additional ones readily released upon applying pressure to the cover glass. Although the scales stained poorly, the addition of a dye such as Orange II was helpful in showing their arrangement. It was clear after staining that the scales overlapped in a manner comparable to the arrangement of shingles on a roof (Fig. 6). Except for a few indistinct markings on the surface, individual scales showed little evidence of internal structure.

When handled with microneedles, groups of scales freed by the action of pepsin appeared to be rather pliable although the individual scale cells were not easily separated from each other. They could, nevertheless, be torn apart in such a way as to form chunks of scale material. In so doing there was no obvious fibrillar structure such as that shown by the cortical cells.

When the Feulgen test for nucleic acid (see section 4) was applied to untreated wool fibers, the scale cells of the shaft gave a negative test. Scales liberated from the fibers by various treatments were also examined in an effort to detect nuclei. Although structures superficially resembling nuclear bodies were observed occasionally in these cells, their presence could not be demonstrated clearly nor consistently.

Scales released by treatment with acids, alkalies, enzymes, or by mechanical scraping were examined between crossed nicols. In all cases, the scales, both before and after staining, showed practically no birefringence.

Additional information concerning the structure of the scales is contained in the section on the Allwörden reaction.

4. Differences between Root and Shaft

Since the cells of the root are alive and growing, whereas the cells of the shaft are dead, it is not surprising to find profound physical and chemical differences between these two regions of the fiber. Several of these differences were revealed when microchemical color tests were applied to wool fibers a short time after they had been carefully pulled from the back of a sheep so as to have the roots attached to the shaft.

These fibers were stained according to Feulgen's technique[11, 12], which is considered to be specific for nucleic acid. A positive test is indicated by the red coloration obtained when a fuchsin-sulfurous acid solution is applied to the nucleus. Fibers which had been given this test showed a root which was stained deep red whereas the shaft remained colorless (Fig. 7). This difference could be detected even with the unaided eye. Upon mounting the stained fibers in a medium or higher refractive index and examining with a microscope, individual nuceli were observed (Fig. 8). At the base of the root the nuclei and cells were relatively large and more or less rounded. Farther from the base the nuclei and cells were elongated.

In some cases the nuclei were very narrow and slit-like, although distinctly red. A little below the level where the fiber emerges from the skin there was a rather abrupt change in the reaction of the nuclei, that is, they gave a negative Feulgen test in the shaft. That this difference did not appear to be caused by poor penetration of the dye into the shaft was indicated by the fact that fibers from which the scales had been removed by mechanical treatment still failed to give a positive test.

In order to study further the changes which take place as the cells pass from the root to the shaft, longitudinal sections were made of pieces of sheepskin with fibers attached. The tissue was embedded in a mixture of paraffin and cellulose[13], cut into sections according to the usual cytological procedure, and then stained either with hematoxylin or according to the method of Feulgen. The cells of the root had a somewhat roundish shape and a more or less granular appearance. The cells of the shaft, on the other hand, were elongated and distinctly fibrous. These facts are undoubtedly related to observations made with crossed nicols, which show that the shaft of the fiber is birefringent whereas the birefringence of the root is negligible. In agreement with the results obtained with single fibers, the nuclei in the cells of the root were found to give a positive reaction to Feulgen's test. Nuclei were observed in those cells of the root which gave rise to scales as well as in those which gave rise to cortical cells.

When a single fiber was mounted in dilute ammonium hydroxide and treated with sodium nitroprusside, a pink to red color was developed in the root, whereas the shaft of the fiber remained colorless (Fig. 9). The red coloration obtained with sodium nitroprusside indicates that at least some of the sulfur in the root is present in sulfhydryl form. This is in agreement with the findings of previous investigators[14, 15, 16, 17, 18] who showed that the sulfhydryl-containing substance is limited to the living cellular parts of the epidermis and its appendages. In order to be sure that the difference in reaction between the root and shaft was not caused merely by a differential rate of penetration of the reagent the scales were mechanically removed from a few fibers. The results with such fibers were in agreement with those obtained in the original test.

Fig. 9—Single fiber (pulled from the back of a sheep) treated with sodium nitroprusside. The dark color of the root indicates the presence of sulfhydryl groups. Part of the cuticle of the follicle remains attached to the fiber.
Magnification X 120

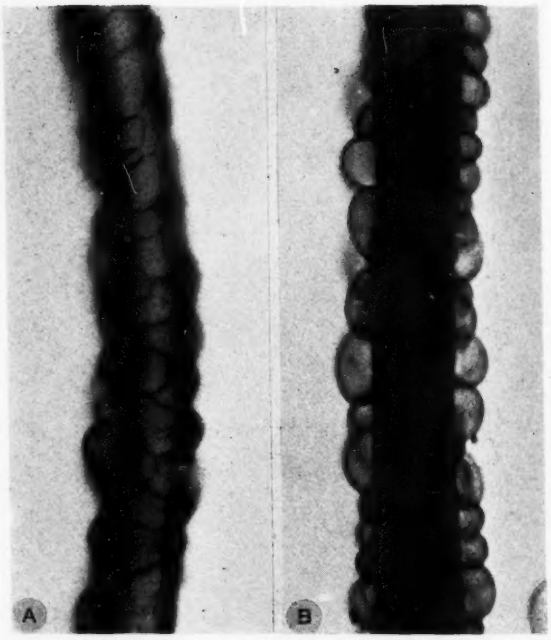

Fig. 10—Fibers treated with saturated chlorine water to give the Allwörden reaction.
A. Surface view of a fiber after sac formation.
B. Fiber in focus approximately midway between its upper and lower surfaces.
Fibers stained with aqueous methylene blue.
Magnification X 500

The biuret test for proteins, the Sakaguchi test for arginine, and the Millon and Pauly tests for tyrosine were also applied to single fibers. These tests did not reveal any differences between the root and shaft, except that the former gave a positive test more quickly.

The differences between the root and shaft may be summarized as follows:

Root	*Shaft*
Soft and easily crushed	Tough and horny
Cells roundish	Cells elongated
Positive test for nucleic acid	Negative test for nucleic acid
Nuclei stained with hematoxylin	Nuclei unstained with hematoxylin
Cytoplasm granular in appearance	Cells distinctly fibrous
Not birefringent	Birefringent
Positive test for sulfhydryl groups	Negative test for sulfhydryl groups
No Allwörden reaction with chlorine water	Many large Allwörden "sacs"*

5. The Allwörden Reaction

When wool fibers are placed in chlorine water the so-called Allwörden reaction takes place[19, 20]. This treatment causes the formation of sacs on the surface of the fiber (Fig. 10, A and B). That the formation of these

*Since the swellings are shown to be protein membranes filled with liquid, "sac" is believed to be a more appropriate descriptive term than "bubble," which is in widespread use in the literature.

Fig. 11—The effect of alkali on Allwörden sacs. Single fiber treated with chlorine water, methylene blue, and then 1 per cent sodium hydroxide, showing the collapsed sac membranes at the surface of the fiber.
Magnification X 500

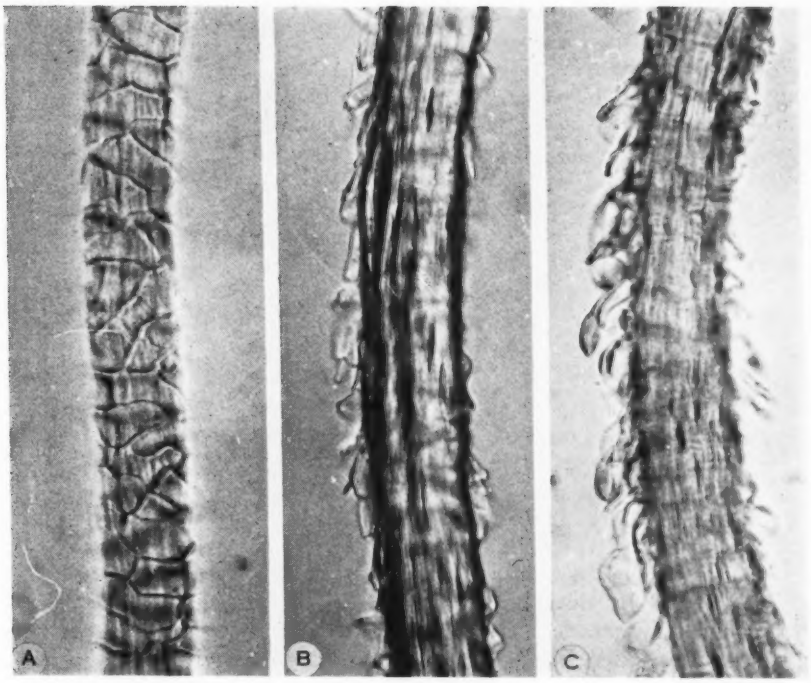

Fig. 12—Scales and their relation to the formation of Allwörden sacs.
A. Fiber mounted in water and photographed in surface view to show the arrangement of the scales.
B. Fiber treated with concentrated sulfuric acid to loosen scales.
C. Fiber treated with sulfuric acid to loosen the scales, and then with chlorine water to form sacs. The photomicrograph shows several sacs in various stages of formation, each arising from an individual scale.
Magnification X 450

sacs is in some way associated with the scales has been suggested by many investigators[19, 20, 21, 22, 23]. It is not clear however from a review of the literature whether the sacs arise solely from the scales, or whether the latter are merely pushed out by the swelling of a layer of material which lies beneath them. Since this is pertinent to an understanding of the structure of the fibers, the reaction was investigated in detail.

Although sacs form quickly with saturated chlorine water, their formation is slowed down by the use of dilute solutions. Likewise, the reaction is retarded, or even completely inhibited by certain types of damage to the fiber. The first evidence of sacs is the appearance on each scale of a small swelling, which gradually increases in size until the sac involves the entire scale surface. Incipient swelling did not appear to be confined to a particular part of the scale, such as base or tip. In a few cases two or more foci of swelling occurred in a single scale and were observed to flow together to form one large sac. It was also evident from the experiments that the size and shape of the sacs was associated with similar properties of the scales.

The sacs usually appeared optically empty. After certain treatments, however, particles showing Brownian movement were observed in them. As described by Kronacher and Lodemann[3], these particles were especially numerous when fibers which had been stained with picric acid were placed in aqueous methylene blue subsequent to their treatment with chlorine water. In agreement with the observations of Kronacher and Saxinger[22], it was found that the thin membrane of a sac could be stroked with a needle of the micromanipulator without causing the sac to burst, but just as soon as the microneedle pierced the membrane the sac collapsed, leaving small bits of the membrane still attached to the fiber. Likewise the sacs collapsed after prolonged treatment with chlorine water, and after exposure to certain chemical agents, especially alkalies (Fig. 11). The sacs were stained by dyes, such as methylene blue and malachite green, and this treatment was helpful in studying their size and shape.

When cross-sections about as thick as the length of the scales of wool fibers were treated with chlorine water, typical sacs were formed. The latter appeared to arise superficially on the surface of the scales. There was no swelling of the region just inside the scales, such as might have been expected if some part of the fiber in addition to the scales was directly involved in the formation of sacs. Although the results of this experiment, as well as some observations with intact single fibers, suggest that the

scales alone give rise to sacs, this fact could not be demonstrated clearly by these techniques.

In untreated wool the scales are closely appressed to one another (Fig. 12, A). In carrying out some preliminary experiments during the course of this investigation, however, it was noted that certain chemical treatments loosened the scales and caused them to bend away from the fiber. For example, when wool fibers were placed in concentrated sulfuric acid for an hour or less, or in concentrated formic acid for several weeks, the scales were loosened in a way which resembled warped shingles on a roof (Fig. 12, B). After prolonged treatment with these acids, single scales, or small groups of scales, were completely separated from the fibers. Scales which had been loosened or liberated in this way were excellent for studying the origin of the sacs. After removal from the acid, the fibers were washed with distilled water and then placed in chlorine water. Sacs formed quickly, and in agreement with the conclusions of Müller[6], it was evident that they came from the scales alone. It was clear, also, that the sacs were formed between the upper and lower surfaces of each individual scale cell. A small swelling first appeared somewhere in the scale, and then increased in size until the whole scale was swollen to resemble a little ellipsoidal bag (Fig. 12, C). Both the upper and lower surfaces of a sac appeared to be of approximately equal thickness. After their formation, the sacs on loose scales showed the same behavior to dyes and chemical reagents as the sacs on fibers which had not been treated with acids. Where the scales were loosened from each other but not bent away from the fiber, the formation of sacs aided in the further separation of the scales. Sometimes sacs were formed on completed isolated scales; at other times where only fragments of single scales were treated with chlorine, sacs were not formed although the two layers of the scale were seen to separate. Apparently in the latter instance true sacs could not form because of the torn edges of the scales. The relationship between the formation of sacs in untreated and in acid-treated fibers is shown diagrammatically in Fig. 13.

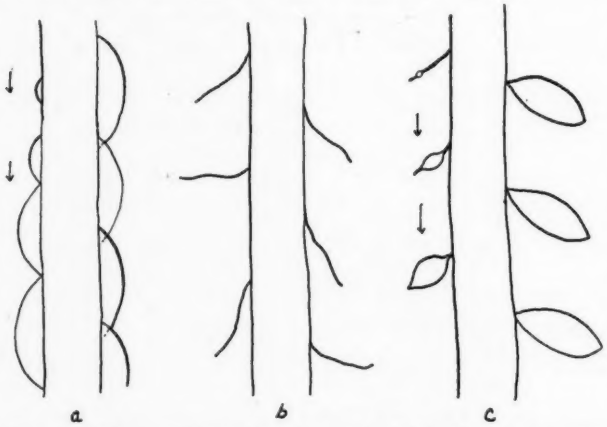

Fig. 13—Diagram illustrating, in longitudinal view, the formation of sacs.
A. The origin of sacs in intact fibers.
B. The separation of scales upon treating intact fibers with sulfuric acid.
C. The origin of sacs on single scales which have been separated by the treatment with acid.
Arrows indicate an increase in size of the sacs.

Fig. 14—Fiber showing root and part of the shaft, after treatment with chlorine water. Many sacs arise in the shaft but none in the root.
Magnification X 120

Chlorine water caused the formation of sacs on all parts of a wool fiber except the root (Fig. 14). Tests on hairs, from more than a score of common and rare animals were, likewise, found to give the Allwörden reaction.

In order to study further the conditions necessary for the formation of Allwörden sacs on the scales, untreated wool was placed in a 0.6 per cent solution of sodium carbonate at 50° C. At various intervals thereafter, samples of the wool were removed, washed in acid and in water, and finally placed in chlorine water. The number, size, and rapidity of formation of the sacs was observed microscopically. It was found that sac formation was retarded with increasing length of alkali treatment. Mark[24] has similarly shown that the number of sacs formed on a fiber by chlorine water was decreased as the concentration of the carbonate and the temperature at which the reaction was carried out was increased. In the present investigation, chemical analysis of the fibers showed that as the cystine content of the fibers decreased, because of the action of the carbonate, sac formation was retarded. Similarly, samples of wool which were degraded by photochemical reactions showed poor sac formation. The extent of the sac formation varied with the duration of the irradiation. Samples of wool degraded in this way also had appreciably reduced cystine contents[25, 26]. The Allwörden reaction was also tried on samples of wool in which

(*Continued on page* 469)

PROCEEDINGS OF THE

American Association of Textile Chemists and Colorists

SEPTEMBER 1, 1941

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Philadelphia Textile School Student Chapter

Joseph E. Dunson, Chairman; Robert J. Wiley, Secretary

Members should notify the **Secretary** immediately of all address changes

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REPORT OF THE NOMINATING COMMITTEE

THE Councilors Representing Sections, in their capacity as Nominating Committee, have directed the Secretary to report the following nominations for the election of 1941:

For President—Thomas R. Smith.

For Vice-Presidents—Roland E. Derby and Charles A. Seibert.

Under the Constitution, additional nominations, each signed by at least twenty-five Senior members, filed with the Secretary not later than October eighth, will be given equal standing on the ballot.

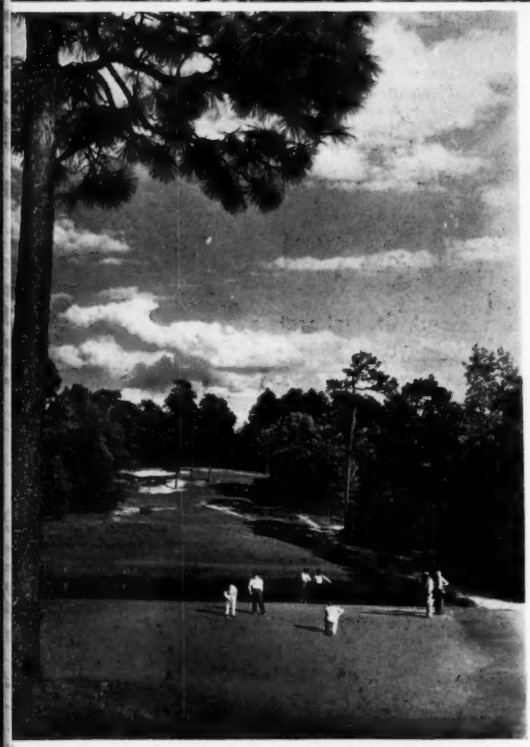
Respectfully submitted,

HAROLD C. CHAPIN, *Secretary.*

ANNUAL MEETING AN

PINEHURST, N. C., OCTOBER

J. D. SANDRIDGE
Chairman, Golf and Tennis Committee



SPORTS PR

Golf and tennis tournaments will be highlights in the sports program at Pinehurst, N. C., during the annual meeting and convention on October 31st and November 1st. It is expected that many of those who attend will participate in these tournaments, which are planned for Saturday afternoon, November 1.

J. D. Sandridge, of the E. I. DuPont de Nemours & Co., Inc., Charlotte, N. C., has been appointed chairman of the golf and tennis committee.

Members of his committee are: Harral O. Pierce, A. Graham McNair, J. Hillman Zahn, L. W. Cleveland, McGee Calhoun, Jr., R. E. Rupp and Norris Rabold.

Golf Tournament

Mr. Sandridge and his committee are planning a most interesting golf tournament on one of three beautiful Donald Ross courses at Pinehurst. Suitable and elaborate prizes for the golf tournament are being provided, and an opportunity will be given for enthusiasts of this sport to compete. Members of the A.A.T.C.C. and guests

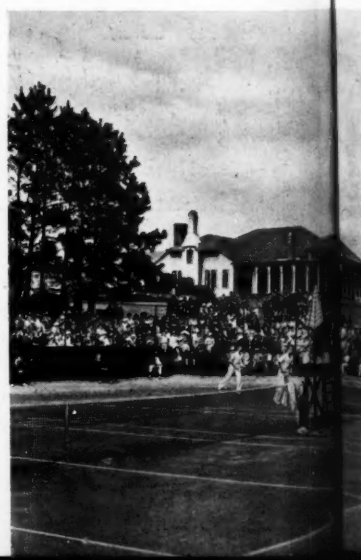
Auspices: Piedmont Section

TOP LEFT—Putting on the second green of No. 3 course at Pinehurst Country Club, Pinehurst, N. C.

CENTER LEFT—Short 14th hole of No. 3 course at the Pinehurst Country Club.

BOTTOM LEFT — Polo grounds and polo ponies in action at Pinehurst.

RIGHT—The clay tennis courts, showing the caddy house and locker room in the background.



NGAND CONVENTION

CTOER 31st—NOVEMBER, 1st

JOE E. MOORE
Chairman, Skeet Committee

TS PROGRAM

will be allowed the reduced green fee of $1.50 for the convention dates.

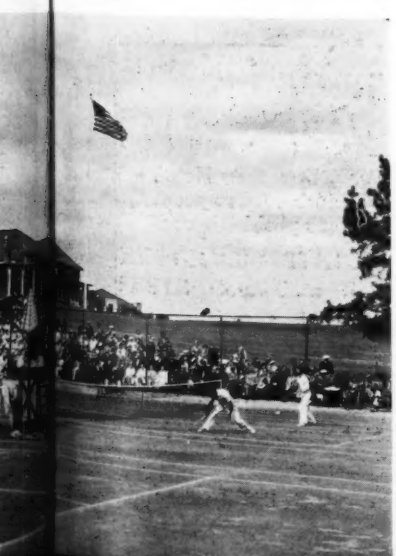
Tennis Tournament

Mr. Sandridge is also in charge of the tennis tournament, which will be featured if there are ten or more contestants. Please write Mr. Sandridge, 412 S. Church St., Charlotte, N. C., if you would like to enter the tennis tournament, so that sufficient and suitable prizes for this event may be selected. Extensive preparations are being made for the various athletic events at Pinehurst, the sports paradise of the South.

Skeet Contest

J. E. Moore, Calco Chemical Co., Charlotte, N. C., is chairman of the skeet committee, which will attract the sharp-shooting members of our association. Bring your gun and compete for the prizes which are being offered in this event. Notify Mr. Moore, Calco Chemical Co.. Wilkinson Boulevard, Charlotte, N. C., if you want to enter this event, so that plans may be completed for the skeet shoot.

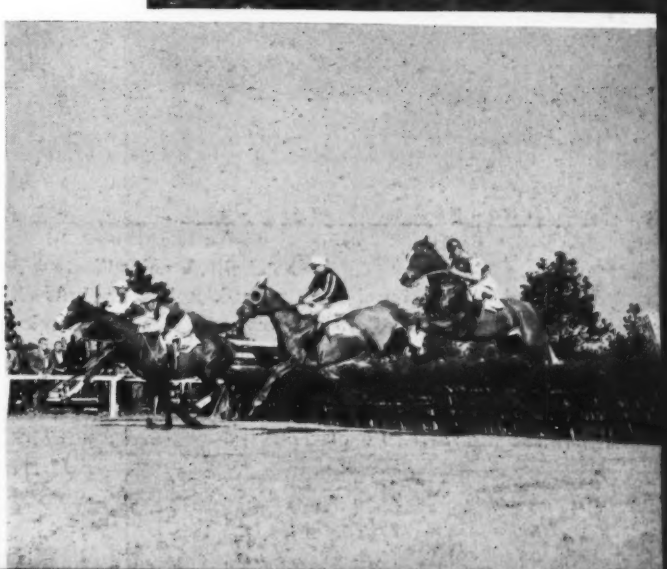
Headquarters: The Carolina



TOP RIGHT—Stands, spectators and contestants in a skeet contest at the Pinehurst Gun Club. Photo by John G. Hemmer.

CENTER RIGHT—One of the beautiful fairways on the famous Donald Ross professional Course No. 2 at Pinehurst. Many national professional tournaments are held here.

BOTTOM RIGHT—A beautiful action picture at one of the hurdles in the Steeplechase, a feature of all sporting events at Pinehurst.

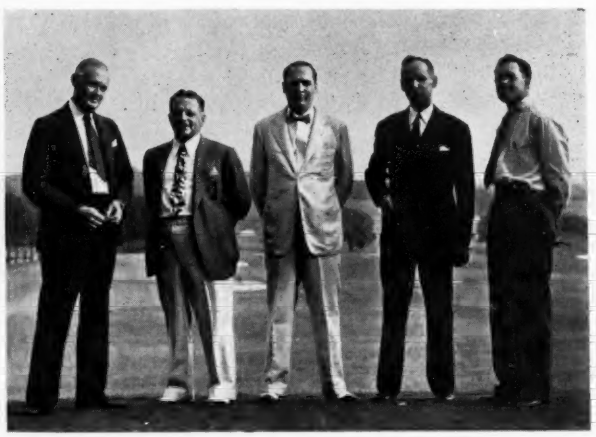


Group photograph taken at the Annual Outing of the Philadelphia Section

OUTING, PHILADELPHIA SECTION

THE Annual Outing of the Philadelphia Section was held on Friday, June 20th, at Whitemarsh Valley Country Club.

We had an attendance of 433 members, 124 of whom play golf, 36 engaged in trap shooting. The Eavanson Cup which is awarded each year to the member of the Section for low gross score was won the second year in succession by J. Phillip of Scholler Brothers, while Walter "Junior" Hamlen of the Du Pont Company was runner-up with a score of 81.



John F. McCoy, Chairman, Philadelphia Section; Arthur E. Jones, Vice-Chairman and Chairman of the Outing Committee; Arthur Etchells, Chairman, Program Committee; George Kohn, Treasurer; William Ebersold, Councilor.

The Outing Committee consisted of Arthur E. Jones, Alco Oil & Chemical Co.; James P. Conaway and R. M. Ritter, Delta Finishing Company; George Kohn, Celanese Corporation; Arthur Etchells, Hellwig Silk Dyeing Co.; Walter Hamlen, Du Pont Company, and William Ebersold, James Lees & Sons.

After a splendid floor show, we distributed 128 prizes to the members and guests who attended this outing.

Respectfully submitted,

J. P. CONAWAY, *Secretary.*

CALENDAR OF COMING EVENTS

Meeting, Southeastern Section, Dempsey Hotel, Macon, Georgia, September 6th, 1941. Program: Round table discussion of various problems concerned with dyeing, bleaching and finishing.

Meeting, New York Section, Chemists' Club, New York City, October 17th, 1941.

Annual Meeting and Convention, Pinehurst, N. C., October 31st-November 1st, 1941.

Theoretical and Practical Aspects of

CATIONIC FINISHING AGENTS

ROBERT R. ACKLEY*

INTRODUCTION
HISTORY AND GENERAL PROPERTIES

THE past few years have seen the development of a new and useful class of textile finishing agents, namely, the cationic finishing, or cation-active softening agents. Originally considered as emulsifying agents, then as agents for improving the fastness of direct dyestuffs on cellulosic fibers, they soon were utilized as finishing agents to impart a soft, smooth hand to textiles. Their rise to popularity for this purpose was indeed rapid, and they are so widely used today as to make it seem evident they are here to stay and will not be displaced. As cationic finishes became more generally accepted, new uses were found, with the result that they are now being employed in a large number of operations, and indications are that even more applications will be developed in the near future. A great amount of experimentation, both on the part of the research chemist and the mill man, has resulted in the discovery of many different methods of utilizing these chemicals for various specific purposes. They are now being used widely on woven rayon goods, both plain dye and printed, on tubular knit goods, in yarn dyeing, and in the hosiery industry. As their properties become understood more generally, their uses in all these fields as well as others will doubtless be increased. In the articles of this series there will be described the background, history, chemical nature, evaluation, and limitations of these materials, as well as specific suggestions for their application in the various fields of textile processing, based on what has been learned from their uses to date.

There is considerable confusion at present as to how compounds of this class should be defined, and even the pronunciation of the various terms has not been completely standardized. Advertising literature has used such names as cationic softening agents, cation-active softeners, permanent softening agents, cationic soaps, and even cat-ion active softeners. It is unfortunate that the term "softener" should be so widely employed to refer to the effect obtained, for it is certain that these materials have a usefulness which extends far beyond mere softening action. By softening, we should mean rendering a fabric more pliable, and, in fact, imparting a certain ragginess. While it is true that this property of many cationic compounds is especially valuable, they are generally used to remove harshness and to leave the fiber with a suedy or waxy touch and to improve the draping qualities as well as the various other intangible properties that make up hand in a merchandisable fabric. It is obvious, therefore, that the term "finishing agent" is more applicable than the misleading designation "softening agent."

The term cation, meaning the portion of a molecule which bears a positive electrical charge in aqueous solution, is properly pronounced cat-í-un, not Kay-shun or cash-yun. The adjective should be pronounced cât-í-ôn-ic. By applying the latter to the term finishing agent, we obtain *cationic finishing agent,* which is probably the most descriptive term for these substances in general.

From a practical point of view, cationic materials may be considered to have properties directly opposed to anionic materials. This distinction becomes simple when we recall that soaps, wetting agents, sulfated oils, and synthetic detergents are classified as anionic. A comparison between the behavior of soaps and cationic finishing agents towards small additions of various agents serves as an illustration.

TABLE I
Comparison of Properties of Soap with Those of a Typical Cationic Finishing Agent

Agent Added	*Effect on Soap*	*Effect on Cationic Finishing Agent*
Hard water	curds	no effect
Glauber salt	no effect	curds
Caustic	no effect	curds
Acetic, formic, or hydrochloric acid.	precipitated	no effect
Aluminum, zinc, chromium, lead, or iron salts	precipitated	no effect
Sulfates, phosphates, etc.	no effect	precipitated
Direct or acid dyestuffs	no effect	precipitated
Soap	.....	precipitated
Wetting agents, sulfonated oils, etc..	no effect	precipitated
Cationic finishing agent	precipitated	.....

We thus see some of the more general properties of cationic finishing agents and their relationship to the properties of soap under the same conditions. At first glance, it might appear that these materials are so susceptible to precipitation as to make their use dangerous, but this ease of precipitation is offset, in the case of the better cationic finishing agents, by the fact that they are sufficiently good emulsifying agents to tolerate small amounts of the materials which cause precipitation. In these cases a small amount of the material is precipitated, but the portion remaining in solution effectively disperses it with no ill effects. It is advisable, however, to avoid contact with those substances listed as causing precipitation wherever possible. The resistance which cationic materials show to

*Industrial Fellow of the Onyx Oil & Chemical Co., Mellon Institute, Pittsburgh, Pa.

precipitation by various chemicals which precipitate soaps, sulfated oils, and the like is actually advantageous, for it makes possible their admixture with certain salts, for example, which could not be employed in conjunction with the older types of finishing agents.

The increasing interest in cationic finishing agents is apparent from data on their use, compared with the total amount of rayon produced in this country. According to reasonable estimates, approximately 20 million pounds of rayon fabrics were treated with cationic finishing agents during 1937, whereas eight times this quantity was treated with such materials in the first six months of 1941. This amounts to over 65 per cent of the total production of rayon (243,000,000 lbs.) in the United States during the same period. The present indications are that the quantity used in 1941 will be about ten times that used in 1937.

THE CHEMICAL NATURE OF CATIONIC FINISHING AGENTS

The complexity of this field is readily appreciated, if we consider the fact that there are, to date, well over a hundred United States Patents for the production and use of several hundred different cationic finishing agents. It is obviously impossible to discuss the chemical nature of these compounds without going deeply into the subject. For a practical understanding of the field, however, it is necessary only to be aware of the characteristic properties of these compounds compared with materials with which we are familiar. For purposes of classification, therefore, we may consider that there are three principal types of cationic finishing agents. The first class consists of the salts of high molecular weight amino compounds. In this class we have the salts of primary, secondary, and tertiary amines. The salts of the tertiary amines are in general more satisfactory for finishing purposes, although they are, unfortunately, more difficult to prepare than the salts of primary and secondary amino compounds. The next class consists of the quaternary ammonium compounds, which are characteristically more stable under operating conditions than the simple salts of amines, although certain particularly complex amine salts possess a stability of the same order as that of the quaternary compounds. The third class consists of "onium" compounds of elements other than nitrogen, seldom encountered in the textile field.

THE DEVELOPMENT OF CATIONIC COMPOUNDS IN THE TEXTILE INDUSTRY

In 1913 Reychler described the soapy characteristics of diethyl cetylamine hydrochloride, one of the first synthetic chemical compounds having soapy characteristics to be prepared. It was regarded for years as a chemical curiosity but was studied by various investigators because of its unusual colloidal properties. In 1925, Hartman and Kagi were granted a U. S. patent on the use of a synthetic cationic material as an emulsifying agent. This material was the salt of a high molecular weight tertiary amine. In 1927, the same two inventors received a patent on the employment of quaternary ammonium compounds derived from the same base, for the same purpose. It was stated in the specification of this patent that the quaternary ammonium compounds had been found to be much more stable and resistant to precipitation than the simple salts of the tertiary amines. The next patents issued in this field were for the use of cationic materials for increasing the fastness of direct dyeings on cellulosic materials to water.

The first cationic finishes sold to the textile trade were in fact intended for this purpose. It soon appeared, however, that, in addition to their dye-fixing properties, certain of these materials possessed the remarkable property of improving the handle of cellulosic fabrics, even when used in very small amounts. Even more surprising was the fact that this effect was resistant to laundering. The use of these compounds as finishing agents grew rapidly, particularly in the solid color dress goods trade, where the use of very small amounts in the last rinse after dyeing produced an effect, which in many cases was greatly superior to that obtained by the use of the more conventional sulfonated oils in a separate finishing operation. By the latter part of 1937, it was generally realized that the use of such materials offered a decided advantage in the finishing of piece goods and that it was actually possible for these chemicals to compete on a price basis with sulfonated oils. The use of such materials has now become general, not only on solid color dress goods, but also on tubular knit goods, hosiery, printed rayon, and pile fabrics. Although it was at first believed that these materials were applicable only to cellulosic fabrics, increasing quantities are being applied to silk and to a less extent to woolens. There are several very good reasons why this new development is an almost indispensable boon to textile processing.

The first and most important reason is that, by the judicious use of a proper cationic finishing agent, the quality of the finished fabric is far superior to that of the same fabric treated with the older type of finishing agent. The finished fabric is more pleasing, not only to the touch, but also to the eye, for there is a marked tendency to reduce break marks and dye streaks which might otherwise occur during processing. The reduction of dye streaks is attributable to a property resembling mordanting, for such finishes tend to prevent bleeding of the dyestuff into folds and creases while the goods are lying wet. The appearance of break marks is lessened because of the greater pliability of the wet yarn during operations such as extraction. Many of the popular fabrics of today, notably those woven from spiral yarns, possess an extremely harsh and sandy handle, even though large amounts of finishing oil are applied. This harshness is greatly reduced when the more effective cationic finishing agents are employed. The finished goods are further improved in respect to the lessening of odor and markoff.

Another reason for the extreme popularity of the cationic finishing agents is the marked economy which their use affords. In general, by the selection of an effective cationic finishing agent, an effect may be obtained which is at least comparable to that imparted by the older type of finishes, but at a substantial reduction in chemical cost.

(*Concluded on Page* 464)

TRADE NOTES • NEW PRODUCTS

• JOINS NOVA CHEMICAL

J. Lindsay Wyman of Augusta, Georgia, has joined the sales force of the Nova Chemical Corporation, as representative for South Carolina and Georgia.

Mr. Wyman's long experience in the textile printing business should prove valuable in his future work. He was employed by the Clearwater Manufacturing Co., Clearwater, S. C., for over ten years in the capacity of both printer and foreman printer, supervising particularly the operation of a high speed printing machine, and also assisted in the development of this apparatus.

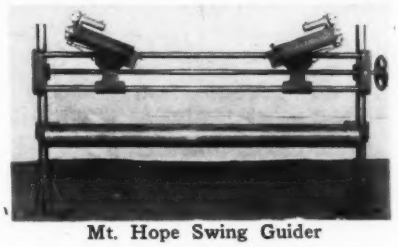
• MT. HOPE GUIDER

Some months ago Mt. Hope Finishing Co., of No. Dighton, Mass., announced that it would manufacture for sale a new mechanical cloth guider and opener, called the Mount Hope Swing Guider. This guider, entirely new in principle, originated in France and was first adopted by Mount Hope Finishing Co. for its own use. When the war made it impossible to get further shipments the Mount Hope Finishing Co. made an exclusive arrangement with the patentee to have similar but improved guiders made in this country and have decided to offer it to the finishing industry.

This business has grown so rapidly that it has been necessary to form a new independent company to take care of it. This new enterprise is known as Mount Hope Machinery Co. and has headquarters at Taunton, Mass. The owner and manager of this company is J. D. Robertson, who was plant engineer for Mt. Hope Finishing Co.

The Mount Hope Swing Guider consists of a pair of heads mounted so that one head operates on one selvage and the second head operates on the other selvage as the cloth passes through it. Each head consists of a rubber covered roll spring-pressed at all times against a mating roll. This pair of small nip rolls is supported from a frame that pivots on ball bearings in such a way that the angle the rolls make with the cloth travel changes automatically to suit requirements. The more the open ends of the nip rolls tip down below the horizontal the quicker they are said to pull the cloth toward their side of the guider. A simple arrangement, without any additional moving parts, swings the nip rolls back upward as the selvage moves toward the inner end and then tips them downward again when the selvage starts to travel toward the outer end of the nip.

The swinging action of the guider frame works on the lever principle. The leverage is applied by the selvage of the cloth as it



Mt. Hope Swing Guider

runs over alternate sides of two stainless steel fingers. It is stated that when the selvage is near the fulcrum or pivot point it exerts comparatively slight leverage, so that a spring keeps the rolls tipped downward in which position they guide the cloth toward their side of the machine. Thus the angle of the rolls determines the position of the selvage and vice versa.

The advantages claimed for this guider are as follows:

1. It is purely mechanical. There are no electric switches or coils to burn out or short circuit and no air valves to get clogged.

2. It is an extremely simple device, having only two moving parts—a pair of revolving nip rolls and a swinging frame. Upkeep is correspondingly low.

3. It has wide adaptability. All types of fabrics from the heaviest to the most delicate can be handled with this device.

4. It provides positive but gentle control. No more control is exerted than is necessary for the particular conditions at the moment.

5. It is rust proof. The rubber covered nip roll is made of brass; the mating roll is also made of brass (rubber covered) or of stainless steel; the frame of tough, durable aluminum alloy; screws are either cadmium plated or stainless steel. Only two parts are made of cast iron and these are painted with three coats of the most durable paint available.

6. It has reversible rubber rolls. That is, when the end of the roll contacting the selvage becomes worn, after long service, it can be reversed, thus giving double life. This is accomplished by unscrewing a single nut.

• pH PAPER DISPENSER

A new and more convenient method of using Hydrion pH Test Papers throughout the range pH 1 to 14 is provided by the plastic dispenser just announced by R. P. Cargille, 118 Liberty Street, New York.

Although "vest-pocket" size, this new dispenser holds and seals two 15 foot rolls of Hydrion pH Test Paper.

When using this new dispenser there is no container to open and close; the user merely pulls out and tears off the test paper needed. Color charts are visible through the transparent walls.

• TRADE NAMES NOW PUBLISHED

The recent announcement that nearly 3,000 trade names which have been in the files of the Trade Mark Bureau of the National Federation of Textiles, Inc., 15 West 37th Street, New York, have been cancelled and consequently are available to other potential users, produced so much interest that it was necessary to make arrangements to sell copies of the list.

It is available to everyone at less than one cent per name and the price includes the privilege of recording 25 trade names with the Bureau without further charge.

• LUCITE CONVEYOR APRON

A conveyor apron made of "Lucite" methyl methacrylate resin rods, which replace brass tubes, is used on the latest textile conditioning machines made by Kearny Manufacturing Company of Kearny, N. J.

This new plastic application is said to release badly needed brass to defense and other vital industries. It is stated that "Lucite" was selected after a year of tests by the manufacturer because of its greater durability and lighter weight.

The plastic conveyor carries different types of bobbins or spools through the conditioning machine. The rods of "Lucite" were manufactured at Arlington, N. J., by the Plastics Department of the Du Pont Company.

• WESTINGHOUSE "STERILAMP"

The United States Testing Company, Inc., has worked out experimental installations of ultra-violet light equipment for the control of mildew and bacteria in the textile, mattress and leather industries.

New ultra-violet irradiating equipment of high intensity, such as the Westinghouse Sterilamp which U. S. Testing Co. is to distribute, is said to offer a definite means of controlling bacteria that may result in spoilage and decomposition of merchandise. It is stated that proper installations of Sterilamps in addition to assuring plant control of micro-organisms will also permit the delivery of more nearly sterile products to the consumer.

The Testing Company will supervise the installation of Sterilamp fixtures by regular plant electricians to make certain that units are placed for proper radiation and maximum kill of mildew and bacteria.

The United States Testing Company has prepared special pamphlets and recommendations for mills and other plants interesting in controlling mildew and bacteria by ultra-violet light.

• NATIONAL DYEING AND FINISHING

The National Dyeing and Finishing Corp. announces the opening of a new dyeing and finishing plant in Los Angeles, Calif., at 935 East 62nd St. The company occupies a new building of approximately 16,000 square feet, equipped for dyeing, bleaching, and finishing with modern equipment purchased from the Van Vlaanderen Machine Company.

The officers are as follows: R. B. Coleman, President; Edwin J. Kraft, Vice President; Earle E. Parkhurst, Treasurer; Hugo Baldecchi, Secretary and Albert Slater, Plant Superintendent.

• DYE-CRETE METHOD

The Wilbur & Williams Co., Park Square Bldg., Boston, Mass., have announced the Dye-Crete Method for coloring and dust-proofing concrete floors. The first part of the Dye-Crete method consists of applying a stain which penetrates deeply into the concrete and becomes a part of it. The second operation makes use of a synthetic enamel which adheres to the stained concrete. Advantages claimed for the Dye-Crete method are as follows: resistance to the action of moisture; resistance to that alkali reaction which, particularly in the presence of moisture, tends to soften any oil paints or varnishes, so that they cannot give a hard, durable finish; resistance to the effects of wear, as even when the concrete wears down, it remains the same color to the depth of the stain penetration; resistance to the effect of oils, greases, alcohol and various other chemicals which attack the usual types of paints.

The first application is a flat finish and the top coating is a gloss. Both Dye-Crete stain and Dye-Crete defensive coating are supplied in four colors: tile red, battleship grey, club green and chestnut brown.

Cationic Finishing Agents—

(Concluded from page 462)

Added to this economy, furthermore, is an appreciable reduction in handling cost. The elimination of extra drying operations has increased the effective capacity of many mills, particularly because of the lessening of congestion at the dry boxes.

HOW DO THESE AGENTS WORK?

It is certainly surprising that such minute quantities of chemicals should bring about pronounced effects on the handle of cellulosic fabrics. Several theories have been advanced to explain the finishing phenomenon, but the mechanism of the effect has not yet been definitely revealed. It is believed by many that the increase in flexibility or softening effect is ascribable to a specific plasticizing action of these compounds on cellulose. According to this view, they behave in the same manner as various chemicals added to synthetic resins to increase their flexibility. The effect on the surface of the fabric, however, is much more interesting, for lubricants of all types have been applied to fabrics, without obtaining the fine waxy surface which we associate today with the use of proper cationic finishing agents. With ordinary lubricants we may increase the concentration until the surface of the fabric is obviously oily and still impart less smoothness to the fabric than when one-tenth as much of a good substantive finish is applied. There must therefore be some difference in the way in which the individual molecules lie on the surface of the yarn. It we consider the shape of the individual molecules of the lubricating oil, for example, we will find that they are long and thin, and that they are of approximately the same construction throughout their entire length.

If we deposit a thin layer of the lubricating oil molecules on a fiber, they will fall in random arrangement, and the thickness of the film will depend upon the number of molecules piled one upon the other. The individual molecules of cationic finishing agent, on the other hand, look more like a cane with a fancy handle, or like a match. That is, one tip of the molecule is distinctly different from the remainder. If we assume that this tip of the molecule sticks tightly to the cellulosic fiber, leaving the remainder free to stand out perpendicular to the fiber, then the apparent thickness of the oily coat on the fabric is about the same as the length of the molecule. In general, for the same amount of material, the oriented cationic finishing agent molecules will give an effective oily coating approximately ten times the thickness of the coating from a lubricating oil. Thus the remarkable affinity of the tip of the molecule for cellulose makes it possible to surround the fiber completely with a thick coating of waxy material, which is attached so firmly that mark-off is impossible.

By this explanation it is obvious that, if the surface of the yarn were already covered by some foreign substance, the full effect of the use of cationic finishes would not be obtained, and this result is indeed true. Thus we come to an important rule in the application of cationic finishing agents. For best surface smoothness, the surface of the yarn should be as clean as possible, prior to the application of the finishing agent. In addition to the lubricating effect on the surface of the yarn, we must also consider the effect on the interior of the yarn, which accounts for the increase in flexibility. Certain types of cationic finishing agents will penetrate quite readily into the interior of the individual filaments. This process is not greatly different from the penetration of dyestuff into the individual filament and, in the same way, requires a certain amount of time. Broadly speaking, it may be said that the higher the temperature and the greater the time allowed, the greater will be the extent of the penetration of the finishing agent into the interior of the yarn, resulting in enhanced softening value. Unfortunately the temperature of application must be dependent upon the properties of the dyestuff used in the prior dyeing of the fabric. Conversely, where the effect desired is primarily surface smoothness, it is desirable to apply the finishing agent at a relative low temperature, to keep the individual molecules on the surface instead of in the interior of the filaments.

NOTE: *Additional articles on this subject by Mr. Ackley will appear in future issues.*—ED.

Division of Cellulose Chemistry of the American Chemical Society

Abstract of Papers to be Presented at Atlantic City, N. J., September 8 to 12, 1941

The following papers will be presented. Those of most interest to textile chemists are given in abstract.

WEDNESDAY MORNING

9:00—1. *Analysis of Cellulose Derivatives. II. The Analysis of Cellulose Mixed Esters by the Partition Method.* Carl J. Malm, Gales F. Nadeau, and Leo B. Genung, Eastman Kodak Company, Rochester, N. Y.

Several methods have been proposed for the determination of the combined acids in mixed esters of cellulose, most of which are based on some physical property of the acids. The differential partition (or distribution) of the acids between immiscible solvents has proved to be a satisfactory and practical means for determining the composition of mixtures of acids. This principle was utilized by Behrens and the manipulation was improved and simplified by Werkman. It has now been applied to cellulose mixed ester analysis, and butyl acetate has been found to be a particularly suitable extractant for mixtures of acetic, propionic, and butyric acids.

The analysis of a cellulose mixed ester by the partition method involves the following steps: determination of total combined acids by some suitable method, saponification and isolation of these combined acids, determination of the partition coefficients between butyl acetate and water of the acid mixture and also separate measurements of the partition coefficients of each of the various acids present, calculation of the molar ratios of the acids using simultaneous equations, and calculation of the weight per cent of the acids, or combined acyl, from the molar ratios and the total acid content of the ester.

Precision, accuracy, and limits of applicability are given. Modifications of the procedure are described for certain higher acyl esters and for non-volatile acid esters.

9:30—2. *A Comparison of the Methods Used to Calculate the Fluidity of Various Cellulose Fabrics Dispersed in Cuprammonium Hydroxide.* Viola C. Jelinek, U. S. Department of Agriculture, Bureau of Home Economics, Division of Textiles and Clothing.

A comparison is made of the different methods of calculating the apparent fluidity of dispersions of various cellulose fabrics in cuprammonium hydroxide over a relatively wide range of values. Cotton and three types of rayon, cuprammonium, viscose, and acetate are the fabrics included. The values obtained with the formulas

$$F = \frac{C'}{t}, \quad F = \frac{C'}{t - \frac{C'}{K}}, \text{ and } F = \frac{q}{C\,(P\text{-}p)}$$

are compared over a fluidity range of approximately 3 to 27 rhes. The graduated type of buret consistometer permitted the calculation of four fluidity values based on a series of observations from four successive 5-ml. portions obtained in one determination and of a single fluidity value obtained from the total 20-ml. quantity. Flow pressure graphs and fluidity-velocity gradient graphs on the same data gave identical information concerning the plastic or true viscous liquid properties of dispersions of cotton, cuprammonium rayon, viscose, and acetate rayon in cuprammonium hydroxide. The deviations of the curves of the flow-pressure graphs of cellulose-cuprammonium hydroxide dispersions from those of true viscous liquids are corrected with the kinetic energy correction and the velocity gradient correction. The range of application of both the kinetic energy and the velocity gradient corrections in the calculations of the fluidity of cellulose-cuprammonium hydroxide dispersions were determined.

9:50—3. *New Methods for Investigating the Distribution of Ethoxyl Groups in a Technical Ethylcellulose.* John F. Mahoney and Clifford B. Purves, Massachusetts Institute of Technology.

The oxidation, with lead tetraacetate, of an ethylcellulose containing 2.48 ethoxyl and 0.52 hydroxyl groups per glucose residue, showed that 0.01 unsubstituted glycol groups were present in the 2:3 position. Quantitative degradation of the ethylcellulose to the corresponding partly ethylated glucoses gave a mixture containing 0.13 to 0.15 mole of glycol in the 1:2 position. The corresponding ethylglucopyranoside mixture had 0.25 to 0.29 mole of glycol distributed between the 2:3 and 3:4 positions. The combined results demonstrated that the ethylcellulose contained 0.13 to 0.15 mole of hydroxyl groups in the second, and 0.24 to 0.28 mole in the third position of the glucose residues.

Sulfur and ethoxyl analyses were used to follow the esterification of the same ethylcellulose with a large excess of *p*-toluene sulfonyl chloride in pyridine. The rate of tosylation of the groups in the sixth position was followed by the iodination technique [Cramer and Purves, J. Am. Chem. Soc., *61*, 3458 (1939)] and subtraction gave the combined rate curve for the second and third positions. This rate curve was the resultant of a fast unimolecular tosylation of 0.151 hydroxyl groups superimposed on the much slower unimolecular reaction of the remaining 0.245 groups. The data, in conjunction with the oxidation experiments, showed that the ethylcellulose had 0.15 mole of hydroxyl group in the second, 0.245 in the third, and 0.124 in the sixth position. The three kinds of hydroxyl group reacted with tosyl chloride with velocities in the approximate ratio of 2.3 to 0.07 to 15, respectively.

10:10—4. *Relationship Between Method of Preparation, Distribution of Substituents, and Solubility in Water or Alkali of Methyl and Ethyl Ethers of Cellulose.* John F. Mahoney and Clifford B. Purves, Massachusetts Institute of Technology.

The tosylation-iodination method indicated in the above abstract was used to estimate the primary alcoholic groups in five other ethers of cellulose and the total number of unsubstituted hydroxyl groups (H) in the second and third positions was obtained by difference. When alkylation occurred with uniform average density along the length of the cellulose macromolecules, the maximum frequency of completely unsubstituted glycol units was calculated to me $H^2/4$. When alkylation was localized in intermittent lengths of the cellulose chain, the probable frequency became $H/2$. The actual occurrence of unsubstituted glycol groups was determined by oxidation with aqueous sodium periodate.

Alkylation of cellulose dispersed in a quaternary ammonium base [Bock, Ind. Eng. Chem., *29*, 985 (1937)] gave a water-soluble product (substitution 0.583) with a glycol content close to $H^2/4$ while the technical, heterogeneous alkylation of alkali cellulose resulted in a water-insoluble product (substitution 0.588) with a glycol count near $H/2$. The other characteristics of the two products were so similar that the insolubility of the latter in water could only be related to the highly non-uniform substitution of the macromolecules.

The primary hydroxyl groups of cellulose were alkylated in a homogeneous system approximately as fast as both secondary groups together. This ratio was smaller in heterogeneous alkylations.

10:45—5. *Fractionation and Molecular Magnitudes of Nitrated Wood.* Edwin C. Jahn and Sydney Coppick, New York State College of Forestry, Syracuse University.

11:15—6. *Hydrolysis and Catalytic Oxidation of Cellulosic Materials. IV. Characterization of Celluloses.* R. F. Nickerson, Mellon Institute of Industrial Research.

The hydrolysis and catalytic oxidation of cellulosic materials with hydrochloric acid—ferric chloride mixture yield carbon

dioxide—time data which, by conversion, give percentages of cellulose hydrolyzed. Since the effective concentrations of hydrolytic and oxidative catalysts in the system are invariant, and since the cellulosic materials investigated contain insoluble, slowly disintegrated residues, the hydrolysis may be regarded as a simple type of liquid-solid interfacial reaction. Calculations based upon this assumption indicate that only a part of each cellulosic material behaves like a homogeneous solid but, by extrapolation, estimates can be obtained of the amounts of homogeneous and non-homogeneous constituents in the intact sample. These, presumably, are crystallite and amorphous components, respectively. The reactivity of the homogeneous or crystallite component can be evaluated also. Such characteristic constants together with moisture regain values for rayon, wood pulp, cotton, mercerized cotton, and industrial linters are presented and discussed.

11:35—7. *The Fractionation of Cellulose Acetate.* A. M. Sookne, H. A. Rutherford, H. Mark, and Milton Harris, Research Laboratory, Textile Foundation, National Bureau of Standards, Washington, D. C.

Through a process of three successive fractionations, cellulose acetate of an acetyl content of 38.6 per cent and an average degree of polymerization of 255 has been resolved into 28 fractions. The fractionation was accomplished by the addition of alcohol to an acetone solution of the acetate. The procedure involved changing of the temperature at constant concentration of the precipitant, and had the advantage of establishing a reversible equilibrium between the material in solution and the precipitate.

The weight-average degrees of polymerization of the fractions varied from 50 to 350. The acetyl content of each of the fractions was identical within the limit of the experimental error. With the exception of the first, all of the fractions were completely soluble in acetone. The first fraction was shown to contain all of the ash of the original acetate solution, and formed hazy, colored solutions in acetone.

Preliminary mechanical measurements on films formed from the different fractions will be discussed.

WEDNESDAY AFTERNOON

Joint Session with Divisions of Organic and Sugar Chemistry

THURSDAY MORNING AND AFTERNOON

9:00—8. *Determination of the Variability of Lignin Content of White Ash.* Elwin E. Harris, Jerome F. Saeman, and M. Y. Pillow, Forest Products Laboratory.

9:30—9. *The Action of Dilute Nitric Acid on Wood Lignin.* Elwin E. Harris and E. C. Sherrard, Forest Products Laboratory.

10:15—11. *Studies of Lignin and Related Compounds. LIII. Isolation of Lignin Building Units: Separation and Isolation of Crystalline 1,2-Diketones.* Marshall Kulka, W. Lincoln Hawkins, and Harold Hibbert, McGill University.

10:25—12. *Studies on Lignin and Related Compounds. LV. Synthesis and Properties of β-Hydroxypropioveratrone.* Kenneth A. West, W. Lincoln Hawkins, and Harold Hibbert.

10:35—13. *Studies on Lignin and Related Compounds. LVI. The Action of Ethanolic Hydrogen Chloride on Lignin Building Units.* Kenneth A. West, W. Lincoln Hawkins, and Harold Hibbert.

10:45—14. *Studies on Lignin and Related Compounds. LVII. The Mechanism of the Ethanolysis Reactions.* William B. Hewson, Joseph L. McCarthy, and Harold Hibbert, McGill University.

10:55—15. *Studies on Lignin and Related Compounds. LVIII. The Mechanism of the Ethanolysis of Maple Wood at High Temperatures.* William B. Hewson, Joseph L. McCarthy, and Harold Hibbert, McGill University.

11:05—16. *Studies of Lignin and Related Compounds. LIX. Aromatic Aldehydes from Plant Materials.* R. H. J. Creighton, Joseph L. McCarthy, and Harold Hibbert, McGill University.

11:15—17. *Studies on Lignin and Related Compounds. LX. High-Pressure Hydrogenation Studies of Maple Ethanolysis Products. Part 1.* Lloyd M. Cooke, Joseph L. McCarthy, and Harold Hibbert, McGill University.

11:30—18. *Studies on Lignin and Related Compounds. LXI. High-Pressure Hydrogenation Studies of Maple Ethanolysis Products, Part 2.* Lloyd M. Cooke, Joseph L. McCarthy, and Harold Hibbert, McGill University.

11:40—19. *Studies on Lignin and Related Compounds. LXII. High-Pressure Hydrogenation Study of Wood.* H. P. Godard, Joseph L. McCarthy, and Harold Hibbert, McGill University.

11:50—20. *Studies on Lignin and Related Compounds. LXIII. High-Pressure Hydrogenation Study of Maple Holocellulose.* John R. Bower, Joseph L. McCarthy, and Harold Hibbert, McGill University.

2:30—21. *The Recovery of Oil from Whole Cotton.* Edward L. Powell and Frank K. Cameron, University of North Carolina.

It is shown that the coloring matters in whole cotton coming from the bark of the stems and cusps can be removed by seeping in an aqueous solution of a soluble sulfide or sulfite; and a commercially practicable recovery of oil from the residue can be effected by solvent extraction.

2:45—22. *The Cellulose Content of Cotton and Woods of Southern Origin.* Wen-Hsien Wan Chen and Frank K. Cameron, University of North Carolina.

The distribution of cellulose in the different components of the cotton plant has been determined and compared with the cellulose content of some typical woods of southern origin.

3:00—23. *The Hemicelluloses of Cornstalks.* H. D. Weihe and Max Phillips, U. S. Department of Agriculture.

3:45—24. *The Sorption of Water by Cellophane.* V. L. Simril and Sherman E. Smith, University of North Carolina.

Four sorption isotherms at temperatures ranging from 16.5° to 49.5° C. have been determined for regenerated cellulose in the form of Cellophane. From these isotherms vapor pressure curves at various equal moisture contents have been constructed. An examination of the log p vs. $1/T$ plot shows that the net heat of sorption is not independent of temperature.

ΔH, ΔF, and ΔS values calculated for the intermediate temperature range show a low entropy (high ΔS) for the water sorbed at low moisture contents. The entropy becomes progressively higher as saturation is approached. Variation in the shapes of the entropy curves for adsorption and desorption points to an essential difference in the two processes. The entropy of the sorbed water on desorption is higher than the adsorption entropy at all moisture contents. The hysteresis loop is interpreted on the basis of the entropy of the sorbed water; the resulting theory is an extension of that of Urquhart. Some conclusions regarding the mechanism of swelling are also reached.

The relationship between moisture regain and relative humidity is discussed. It is shown that the regain is independent of the temperature only when $\Delta H = 0$.

4:10—25. *Some Properties of Cellulose Esters of Acetic, Propionic, and Butyric Acids.* C. J. Malm, C. R. Fordyce, and H. A. Tanner, Eastman Kodak Company, Rochester, N. Y.

Physical properties of both the simple and mixed cellulose esters of acetic, propionic, and butyric acids are presented, showing variation in properties with changes in acyl group and degree of esterification.

The importance of these properties, including melting point, specific gravity, moisture absorption, solubility, and plasticizer compatibility, in indicating the usefulness of the cellulose esters is considered.

• TECHNICAL NOTES FROM FOREIGN SOURCES •

Dissociation of Ammonium Salts in Contact with Wool—3

Goodall and Hobday—J. Soc. Dyers & Col., 56-384, *Sept.*, 1940.—The present article is the third of a series on this subject, the two earlier ones having been mentioned in these columns during the past year. The examination of the dissociation properties of a number of ammonium salts covered in the previous papers gave results of interest both as regards practical dyeing and the general theory of behavior of ammonium salts in relation to wool. These results, however, were obtained under restricted experimental conditions, which the authors felt it desirable to extend very considerably.

After sketching the generalized theory of the subject, of which a considerable portion has been experimentally verified by the work described in Parts 1 and 2, and noting the need for further experimental evidence under more extreme conditions, the authors call attention to the fact that the theoretical conception they have outlined is at variance with the views and experimental results of Porai-Koschitz, who has published several articles on this subject during recent years. To check the widely accepted findings of this author was regarded by them as an important part of their investigation.

The work of Porai-Koschitz is reviewed, and points in it against which the authors feel criticism may be offered are specified. These are (a) the purification process applied to the wool used, (b) the claim to have reached stages in each experiment where ammonia ceased to volatilize and (c) the two assumptions that increased development of acid, measured by increased ammonia volatilization in the presence of wool, was (1) completely sorbed by wool and (2) consisted entirely of dye acid. As it was believed that these claims rest on unreliable experimental evidence and an incomplete theoretical approach, it appeared desirable that the work of Porai-Koschitz should be reinvestigated with more careful and more reliable experimental technique.

Experiments were therefore carried out with the first object of confirming the general theoretical conceptions outlined by the authors as regards the effect of concentration of ammonium salts and as regards the difference in behavior of ammonium salts of strong acids and those of weak acids under conditions of extended treatment at the boil. The next stage of the investigation was the establishment of the further theoretical conception that any ammonium salt solution containing two anions would behave substantially like a solution of the ammonium salt of the weaker anion present. The final stage consisted of an examination of similar systems in which the second anion was introduced as the sodium salt of a dye. Throughout the experiment it was desired to check the findings of Porai-Koschitz, particularly in his opinion that a stage of equilibrium can eventually be reached in a boiling ammonium salt solution, both in presence and absence of wool, and also one of his basic hypothesis to the effect that an increase in the amount of ammonia volatilized in the presence of wool corresponded exactly with the amount of acid or dye combined with the fiber.

There is then described a series of carefully controlled experiments in which the liberated ammonia was determined during the extended boiling of ammonium salt solutions, alone and in contact with both wool and dye. The boiling period was generally carried to 30 hours, in at least one case to 66 hours. Curves are constructed to show amounts of ammonia evolved in relation to time of boiling, and other observations are expressed in a series of tables. Conclusions drawn from this investigation may be summed up as follows:

In solutions of constant ammonium concentration, the rate of evolution and the total quantity of ammonia evolved are functions of the dissociation constant of the acid from which the salt is derived, i.e., a salt of a weak acid shows initially and maintains a markedly higher pH and a consequently higher evolution of ammonia than a salt of a strong acid. Where the solution contains two anions, the behavior approximates to that of an ammonium salt of the weaker anion present.

The effect of introducing wool into such solutions is also dependent upon the dissociation constant of the acid from which the salt is derived. Owing to acid sorption by the wool, the introduction of wool into the solutions of salts of strong acids causes a marked increase in evolved ammonia; with solutions of salts of weak acids the introduction of wool is without effect on ammonia volatilization.

These conditions apply to systems where the probable reaction with wool is purely chemical and shows little interference from physical effects. Such purely physical effects become pronounced when one of the anions present consists of a dye anion. In the absence of wool, systems containing ammonium chloride and dye behave almost identically with systems of ammonium chloride alone; in systems containing both wool and dye the physical effect causes a shift in the equilibrium balance of the system in the direction of the fiber holding a greater proportion of dye anion and corresponding H^+ ions than would be the case in the absence of dye. The presence of dye consequently results in an increased volatilization of ammonia, and the amount of dye-acid sorbed by the wool is in such cases much larger than is equivalent to the additional ammonia evolved as the result of the introduction of wool.

The theoretical conceptions put forward and their experimental confirmation have been shown to be at variance with the views and experimental results of Porai-Koschitz in that they disprove two fundamental assumptions made by this author in similar experiments—that systems of ammonium salts and wool can reach a state

equilibrium after prolonged boiling, and that any additional ammonia evolved in consequence of the presence of wool is equivalent to the acid, whether colorless or dye-acid, sorbed by the wool.

On these assumptions, this author stated that all dye-acids combine with wool in stoichiometrically equivalent portions, but it has now been shown that this statement is founded on faulty experimental technique and an incomplete theoretical approach.

A Colorimetric Method of Determining Indigo

J. Lotichius—J. Soc. Dyers & Col., 56-433, *Oct.*, 1940.—The author has previously described (J. Soc. Dyers & Col., 1939, 55-87) a colorimetric method of determining the Indigo content of Indigo vats, based on the property of Indigo of appearing in the form of a stable blue sol when sodium protoalbinate is added to an alkali solution of leuco-Indigo and the latter oxidized. This method cannot be applied as it stands for determining Indigo itself because losses are liable to occur during reduction. Conditions are now described under which this reduction proceeds quantitatively, rendering it possible to determine Indigo itself colorimetrically.

A sample of approximately 0.25 gr. of Indigo is weighed and put into a 250 cc. graduated flask, together with 100 cc. distilled water, 10 cc. 85°Tw. caustic soda, 7 cc. sodium protoalbinate solution (previously described) and about 2.0 gr. sodium hydrosulfite powded. The flask is sealed air-tight and contents allowed to reduce for several hours, or best over night, at room temperature (not exceeding 30° C.). When all the Indigo has been reduced, the solution is oxidized by adding a few cc. of 30 per cent hydrogen peroxide and a blue color is produced. The mixture is made up to 250 cc., diluted as necessary, and checked against a standard solution, which is prepared as previously described from Sirius Blue B and Sirius Green 2B.

The accuracy of this method was checked by applying it to weighed amounts of pure Indigo, specially prepared, and the determinations found to be in good agreement. It has also been found possible by its use to determine accurately the Indigo content of Indigo printing pastes.

Alginic Acid Rayon from Seaweed

Jour. Text. Inst.—XXXII, 1, 2, *Abstracts, Jan., Feb.*, 1941.—During the past year there were published several articles by J. B. Speakman (Textile Weekly, 26-636; Textile Mercury and Argus, 103-512; Textile Manufacturer, 66-464) describing the production and properties of a new rayon consisting of metallic alginates.

Alginic acid, the raw material for this product, is readily extracted from seaweed, which contains 20-30 per cent of the acid, by treatment with sodium carbonate solution. It is a polymer of *d*-mannuronic acid, and its long-chain molecules carry free carboxyl groups at regular intervals along their length. A solution of sodium alginate can be extruded through spinnerets into a suitable coagulating bath in the manner of viscose rayon.

Alginic acid and the simple alginates are soluble in soap and soda solution, and therefore useless as textile fibers, but certain metallic alginates, preferably the beryllium salt, have been found resistant to alkalis. Such filaments are of high luster and of good strength, which may be improved by stretch spinning; because of their high metallic content the alginate fibers are fireproof, and accordingly well suited to use in furnishing fabrics. The fibers have a high affinity for water, rather greater than that of wool, and should thus be useful for the manufacture of underclothing.

The carboxyl groups present should give this rayon good affinity for basic dyes, and also facilitate the even distribution of delustering salts in the filaments. Dyeing properties of the alginate yarns may be varied at will, in accordance with the metals used in producing them. The raw material is abundant and cheap, seaweed in former years having been collected to the extent of 400,000 tons annually in the Hebrides.

The Fluidity of Silk Solutions: Measurement and Application

*Garrett, Howitt, Cadwallader and Smith—Jour. Tex. Inst., XXXII-T*1, *Jan.*, 1941.—The determination of the fluidity of cellulosic material in a cuprammonium solvent has proved of such value in the assessment of the chemical degradation of cotton and rayon materials that need has been indicated for an analogous test applicable to silk. Up to the present time only one such method for the differentiation of chemical and mechanical damage in silk has been published, a process depending on the use of a concentrated solution of zinc chloride as a solvent for silk, which is not regarded by the authors as entirely satisfactory.

An extended examination was therefore made of all reagents known to dissolve silk with regard to their applicability to a fluidity test for silk. One of these, cupri-ethylenediamine solution, appears to be of outstanding merit. Though it suffers from the disadvantage of degrading the dissolved silk at a significant rate, the degradation is almost eliminated by neutralization of the cupri-ethylenediamine complex after dissolution of the silk.

The method finally adopted is that of dissolving silk in a reagent containing 8 per cent ethylenediamine and 6 per cent of cupric hydroxide to give a solution 10 per cent (weight/volume) in silk, calculated as dry weight; this solution is neutralized with an equal volume of acetic acid (to give a solution 5 per cent in silk) and the fluidity is determined by use of a U-tube type viscometer.

Measured by the method described, the fluidity of a solution of untendered silk is approximately 4 reciprocal poises, while for silk chemically tendered to an extent corresponding with almost complete loss of strength, the fluidity is approximately 50. Expressed alternatively in viscosity units, the range is from about 25 to 2 centipoises. As a result of this wide (12-fold) range, a sensitive measure of chemical tendering is obtained that does not require very great accuracy in the measurement of the rate of flow.

The paper describes in detail the selection and preparation of the silk solvent, specifications of the viscometer employed and general technique of this method of measuring the fluidity of various silk solutions. A curve is constructed to show the rate of change of fluidity on standing of a 5 per cent solution of silk at different values of pH, and the fluidities determined for solutions of tendered and untendered silk at different concentrations of silk are presented in tabular form.

In a separate paper (Cadwallader, Hewitt and Smith) is considered the relationship existing between fluidity and tensile strength of silks tendered to varying extents and by different chemical reagents, and also the value of fluidity determinations in appraising the approximate retentions of strength by silk yarns or fabrics which have experienced chemical treatment parallel to that operating in commercial practice.

In addition to the economy in time and material that the fluidity method has over the direct examination of tensile strength, the determination of fluidity considerably amplifies the somewhat limited information given by determinations of breaking load. The loss in strength of silk due to chemical degradation of fibroin occurs in a more insidious manner than does that due to mechanical degradation. It is hoped that the present fluidity test for silk will at least partly fulfill the requirement for a test for chemical damage which can be readily applied and is of adequate sensitivity. At present this fluidity test is applicable to degummed silk and to silk which has been degummed and dyed; it cannot be applied directly to tin-weighted silk owing to the formation of a gelatinous precipitate on dissolving in the cuprietheylenediamine reagent.

A large number of fluidity determinations was made on silk material of different types, including raw filature and waste, yarns, parachute fabrics, commercial fabrics and hosiery. Values determined for these materials, expressed in reciprocal poises at 20° C., are presented in a series of tables. An examination is made of silk yarn treated with acid and alkali solutions for varying periods of time, and the relations between fluidity and percentage loss in strength of the yarn so treated are given in graph form. The effects of heat and of light upon silk, in relation to its fluidity, are also discussed.

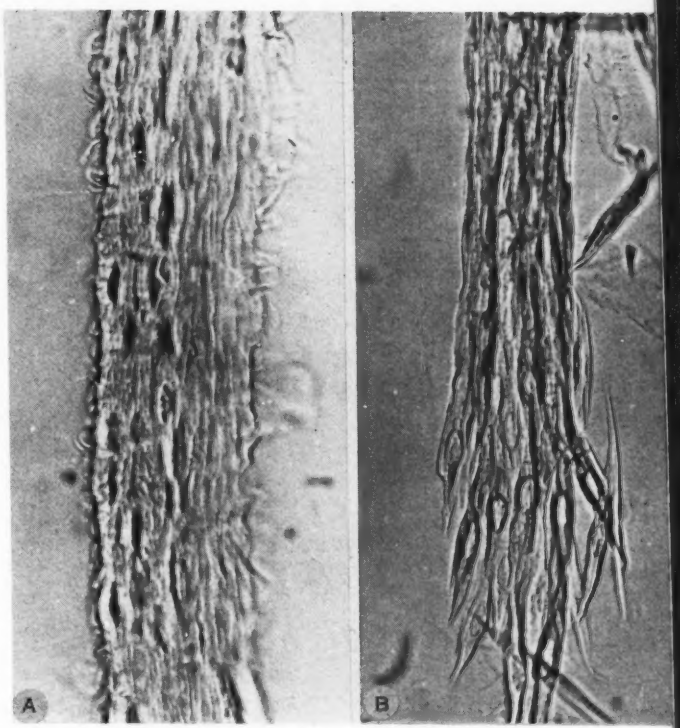


Fig. 15—Fibers showing swellings in the cortex after treatment with acid and chlorine water.
A. Wool fiber after 2 hours in concentrated sulfuric acid followed by treatment with chlorine water.
B. Wool fiber after 14 months in concentrated formic acid followed by treatment with chlorine water. Similar results were obtained with fibers that had been boiled in the acid for about 4 hours.
Magnification X 450

Wool Fiber

(Continued from page 456)

the mode of linkage of the sulfur had been altered by treatments such as reduction and alkylation. In all cases the sacs were formed more quickly when the cystine content was high, whereas the formation of sacs did not occur when the cystine content was lowered sufficiently. While not all of the above chemical treatments are specific for cystine in wool, it is significant, nevertheless, that samples of wool with low cystine contents fail to give the Allwörden reaction. The results suggest that the formation of sacs is dependent on the specific reaction of chlorine with unaltered disulfide groups of the cystine in the scales of the fiber. That chlorine can react with cystine has already been demonstrated[27]. A possible mechanism is that the disulfide linkages are split and oxidized to strongly acid groups such as perhaps sulfonic acid groups. An osmotic type of swelling could then take place to form the sacs noted. Further evidence favoring this view is obtained when concentrated salt solutions are added to the fibers after the reaction with the chlorine. Under these conditions the sacs contract.

It was noted, during the course of the above experiments with acid-treated wool, that when the scales give rise to typical sacs, localized swellings often appeared in the cortex (Fig. 15, A, and B). In order to study this phenomenon further, wool fibers were treated with acid for longer periods in order not only to loosen the scales but to release individual cortical cells as well. Fibers which had been placed in concentrated sulfuric acid at room temperature for 1 to 2 hours, or in boiling concentrated formic acid for about 6 hours, were found to be suitable for these experiments. Individual cortical cells released by these treatments showed distinct signs of swelling when placed in chlorine water. It was obvious, moreover, that the swelling in each cell was confined principally to the nucleus (Fig. 15, B and 16). In

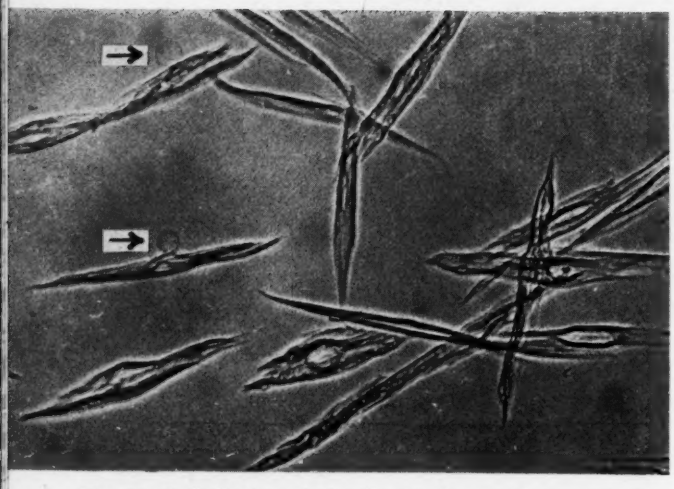


Fig. 16—Individual cortical cells showing swollen nuclei after treatment with chlorine water.

The cells were released by the prolonged action of concentrated formic acid, and then, after washing in distilled water, treated with chlorine. Arrows indicate additional swellings which sometimes arise from the nucleus.

Magnification X 420

some cases additional swellings appeared to arise as buds from the swollen nucleus (Fig. 16). Swollen nuclei were not observed in fibers which has been treated with alkali or other reagents which prevent the Allwörden reaction. Although the foregoing observations suggest that the typical Allwörden reaction of the scales and the swelling cortical nuclei may be related phenomena, additional experiments pointed to dissimilarities between the two. In the presence of concentrated salt solutions, for example, the scale sacs become flaccid, and upon replacing the salt solution with water they regained their former turgidity; the nuclear swellings on the other hand failed to react in his way. Furthermore, a gentle prick with the tip of a microneedle was sufficient to bring about the collapse of scale sacs, whereas this did not occur when nuclear swellings were punctured.

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